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## SOLID-PHASE PROCESSES IN A CERAMIC MATRIX IN THE SYSTEM $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{TiO}_2$ WITH ADDITION OF FIBROUS NANOSTRUCTURAL ALUMINUM OXIDE

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The formation of a composite ceramic based on the system  $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{TiO}_2$  with the addition of  $\gamma$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$  nanostructural powders during heat treatment in the temperature range 1300–1400°C is investigated. It is established that the introduction of  $\gamma$ - $\text{Al}_2\text{O}_3$  reactive nanostructural powder stimulated a solid-phase reaction between the silica and alumina with mullite being formed, while the addition of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder led to the formation of aluminum titanate. These processes altered the phase composition and the porous and crystalline structure of the composites and increased their physical–chemical and thermophysical properties.

**Key words:** ceramic, solid-phase processes, additives, nanostructural aluminum oxide.

The production of new types of articles from ceramic composites, the diversity of the conditions under which they are used in machine engineering and the chemical industry, the continually growing requirements for operating characteristics of machines, mechanisms, and thermal equipment all make it necessary to develop new composite materials with improved and special properties — increased porosity, stiffness, durability, heat-resistance, and thermal-shock resistance [1].

One of the main characteristics of refractory ceramic materials used in high-temperature engineering is their capability of withstanding thermal shocks without breaking down while retaining high mechanical and thermophysical properties. The CLTE has a considerable effect of the resistance of ceramic materials to thermal shock. Examples of such materials are ceramics based on aluminum titanate — tialite  $\text{Al}_2\text{TiO}_5$ , which has a low CLTE, high thermal shock resistance and heat resistance, and good resistance to corrosion. However, the use of tialite is limited by its low mechanical strength and low thermal stability at temperatures 750–1350 and above 1600°C, as a result of which it decomposes into metal oxides [2].

Silicon, iron, zirconium, chromium, and other metal oxides are usually added to ceramic to increase the thermal

shock resistance of ceramic and improve its properties [3]. The ternary system  $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{TiO}_2$  with different ratios of the components, which is used to manufacture mullite-tialite ceramic, is most often used in practice [4, 5]. However, it is quite difficult to obtain the optimal composition with the highest possible physical-mechanical and thermophysical characteristics, since a composite ceramic must be reinforced or its density increased in order to strengthen it. At the same time the thermophysical properties are due to the porosity of the material and the presence of a low-expansion tialite phase.

Analysis of recent publications has shown that the methods used to obtain pure aluminum titanate and its solid solutions with metal oxide additives which possess stable operating characteristics require further study and materials testing.

We used natural and commercial powders to obtain an inexpensive ceramic composite; reactive fiber nanostructural aluminum oxide powder, which could affect the solid-phase reactions of the three-component system and change its physical–mechanical and thermophysical characteristics, was used as the nanostructural filler.

The ratio of the oxides in the matrix of the system  $\text{SiO}_2 - \text{TiO}_2 - \text{Al}_2\text{O}_3$  was 35 : 35 : 30%.<sup>4</sup> According to the phase diagram this ratio of the components falls in the crystallization field of the mixture of mullite and tialite phases [6, 7]. “Granitik-Vesko” clay from the Veselovskoe deposit,

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<sup>4</sup> Here and below — content by weight.

GK technical grade alumina, reactive pure titanium oxide, and synthesized fibrous nanostructural  $\gamma$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$  powders were used to prepare samples of the matrix and composites.

Cellulose hydrate (viscose) filaments served as the initial materials for obtaining oxide nanocrystalline fibrous powders. Commercial impurities were removed from the filaments, which were permeated with a water solution of aluminum chloride, dried, and heat-treated at 700–1200°C. Oxide filaments were ground in a mill with porcelain balls and sifted using calibrated sieves.

The fibrous powder consisted of white needle-shaped particles, themselves consisting of two types of nanocrystallites:  $\gamma$ - $\text{Al}_2\text{O}_3$  (700°C) and  $\alpha$ - $\text{Al}_2\text{O}_3$  (1200°C). The  $\gamma$ -phase of aluminum oxide possessed cubic structure, the crystallites were 6–7 nm in size, the bulk density of the oxide was 0.46 g/cm<sup>3</sup>, the pycnometric density was 2.94 g/cm<sup>3</sup>, and the specific surface area was 120 m<sup>2</sup>/g approximately. The size of the crystallites of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder did not exceed 50–55 nm, the bulk density was 0.54 g/cm<sup>3</sup>, the pycnometric density was 3.75 g/cm<sup>3</sup>, and the specific surface area was 30–35 m<sup>2</sup>/g [8]. The filler content in the mix ranged from 5 to 20%.

Samples of the matrix of the system  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$ – $\text{TiO}_2$  and composites with fillers were prepared by the conventional ceramic technology by means of semidry pressing from moistened slip mix of the powders. The samples were dried at 120°C and heated in an electric furnace to 900–1100°C first, after which they were subjected to isothermal firing at 1300, 1350, and 1400°C for 2 h.

The crystalline structure of the composite ceramic materials was investigated and their phase composition was determined with DRON-2 and -3 x-ray diffractometers. The diffraction patterns at angle  $2\theta$  ranging from 5 to 110° were recorded in a computer at rates 0.5 and 1.0 °/min. Monochromatized  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) was used. A JCPDS card file was used to identify the crystalline phases. The integral intensities of the reflections of the metal oxide phases obtained from the x-ray diffraction patterns were evaluated with an external standard according to the following reflections:  $\text{TiO}_2$  (rutile) — 27.447° (110), 36.086° (101);  $\alpha$ - $\text{Al}_2\text{O}_3$  — 25.459° (012), 43.241° (113);  $\alpha$ - $\text{SiO}_2$  — 20.850° (100), 26.652° (101);  $3\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3$  (mullite) — 16.443° (110), 33.229° (220), 40.875° (121);  $\text{Al}_2\text{TiO}_5$  (tialite) — 18.809° (020), 47.853° (043), 50.825° (200). The microstructure of surface of the fibrous materials and the composite ceramic was studied with a Leo 1420 scanning electron microscope ( $\times 500$ – $1000$ ). The samples of the materials were coated with gold. The measurements were performed with voltage 20 kV; the resolving power of the microscope was 10 nm.

The density, porosity, water absorption, and linear shrinkage were measured by standard methods. The heat shock resistance was evaluated by the number of heat changes with temperature differential 800–10°C (GOST

7875–94). This method consisted in determining the number of cycles including heating samples at 800°C in 30 min and their subsequent cooling in a stream of water from 10°C to the appearance of the first cracks.

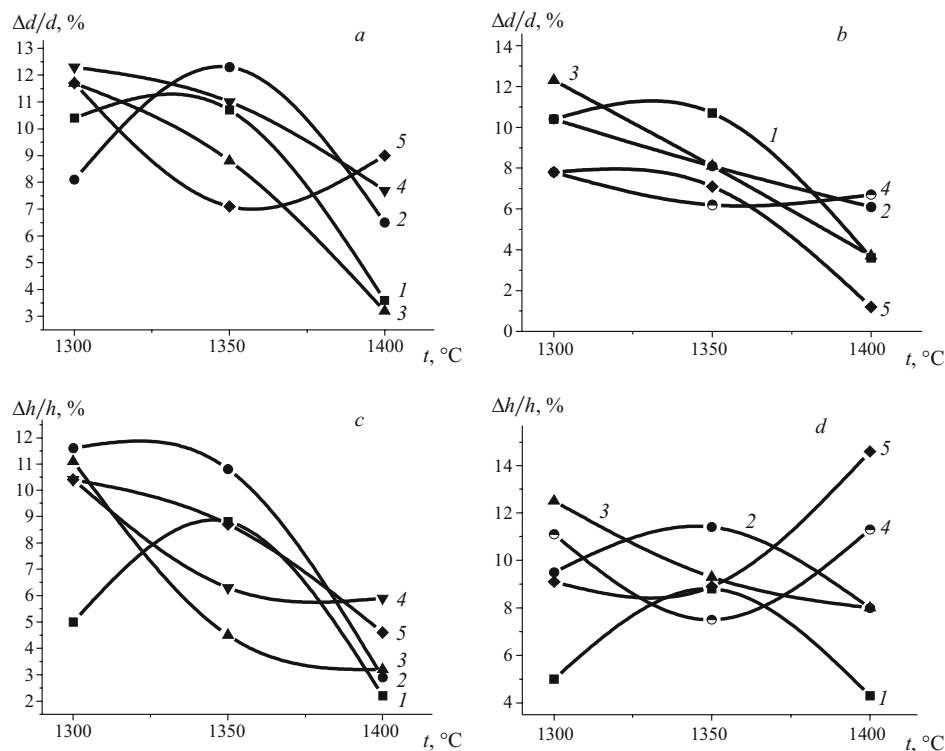
The determination of the linear dimensions of sample of the matrix and composites fired at 1300–1400°C showed that shrinkage decreased with increasing temperature. This anomalous behavior of the samples during heat treatment is due to the melting of silicate glasses, forming from alkali and alkaline-earth compounds present in clay and silicon oxide. The melt filled the pore space, less shrinkage of the material occurred during cooling, and shrinkage was nonuniform along the height and diameter of the samples. Thus, for the matrix the shrinkage after firing at 1300°C was 5% along the height and 10.5% along the diameter, while after firing at 1400°C the shrinkage was 2.5 and 3.5%, respectively (Fig. 1).

As a result of its high porosity and extended surface area the reactive  $\gamma$ - $\text{Al}_2\text{O}_3$  fibrous powder interacted with the glass melt, and the shrinkage along the diameter at 1400°C increased very little only with 20% filler added. The addition of nanostructural fibrous  $\alpha$ - $\text{Al}_2\text{O}_3$  powder in small quantities (5–10%) into the system had no appreciable effect on the shrinkage of the composites; the introduction of 10 and 20% filler increased the consolidation of the material. As a result, the shrinkage along the height of the sample increased with increasing firing temperature. On the whole, for heating above 1300°C the structure of the material consisted of a mixture of phases: crystals of metal oxides and their interaction products as well as the fibrous particles introduced and the glassy silicate mix (Fig. 2).

As x-ray phase analysis of the crystal structure of the matrix and composites has shown, the integral intensities of the reflections of the initial and formed phases in the composites depended on the amount of the reactive additive of nanostructural aluminum oxide powders introduced, its crystal temperature, and the heat-treatment temperature of the blanks.

After the samples of the matrix were fired at 1300°C the phase composition of the matrix consisted of a mixture of rutile, mullite, and an admixture of  $\alpha$ -corundum. When the firing temperature was increased to 1350°C, aside from rutile and mullite a very small amount of tialite,  $\alpha$ -quartz, and  $\alpha$ -corundum appeared. After firing at 1400°C the main phases were rutile and mullite and the impurities were tialite and  $\alpha$ -quartz. When  $\gamma$ - $\text{Al}_2\text{O}_3$  nanostructural powder was introduced, mullite formed near 1300°C and rutile and traces of  $\alpha$ -corundum were present, but no interaction between  $\gamma$ - $\text{Al}_2\text{O}_3$  with titanium oxide occurred.

As temperature increased to 1350°C, the intensity of the mullite reflections increased in proportion to the increase in the content of the active filler, which confirms the priority of this solid-phase reaction in the system, and a tialite phase appeared (Fig. 3). A reaction forming aluminum titanate occurred during heat treatment of samples of a composite with



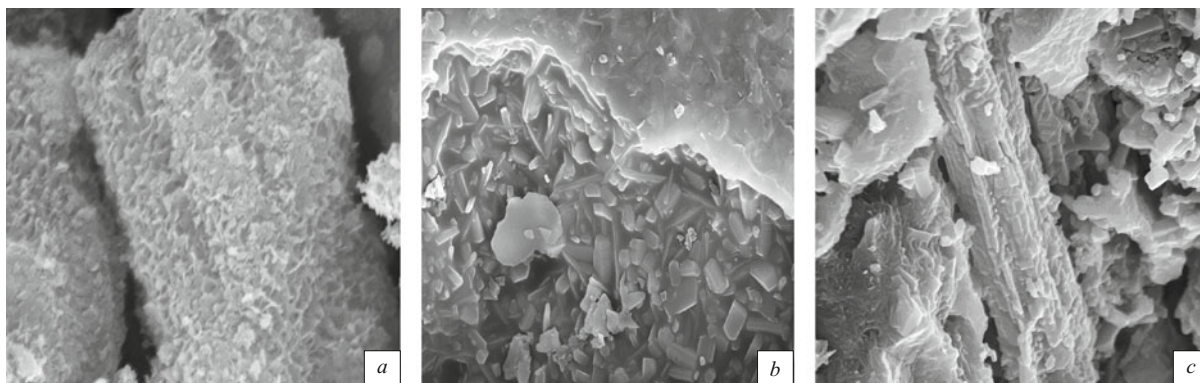
**Fig. 1.** Shrinkage along the diameter (*a, b*) and height (*c, d*) of samples of the matrix and composites with addition of  $\gamma\text{-Al}_2\text{O}_3$  (*a, c*) and  $\alpha\text{-Al}_2\text{O}_3$  (*b, d*) nano-structural fibrous powder versus heat-treatment temperature: 1) matrix, 2, 3, 4, and 5) 5, 10, 15, and 20% content of additive, respectively.

added  $\gamma\text{-Al}_2\text{O}_3$  at 1400 °C; the intensity of its reflections increased and that of rutile decreased sharply, which is due to its interaction with aluminum oxide.

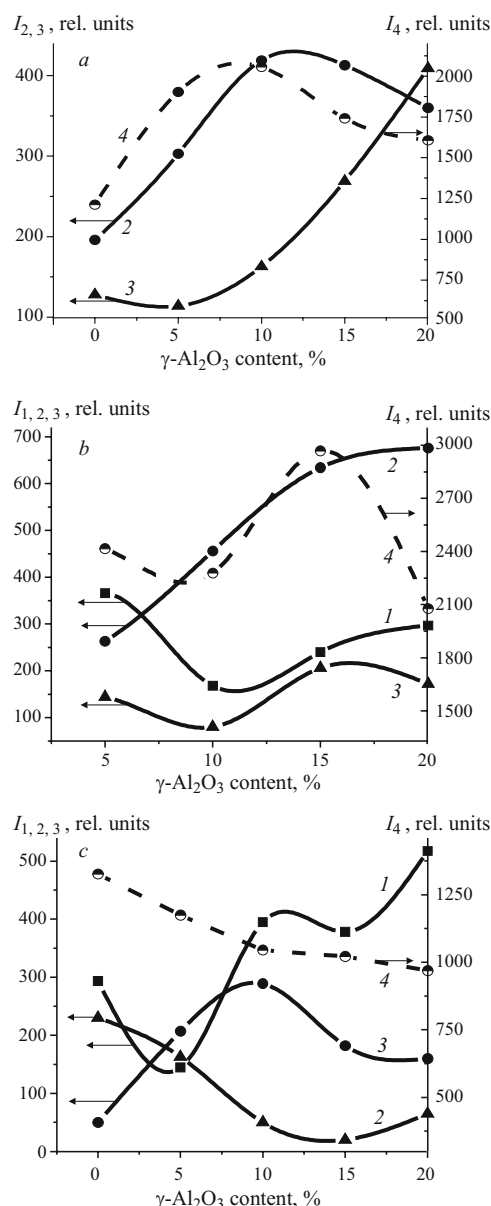
When active  $\alpha\text{-Al}_2\text{O}_3$  powder was added to the matrix, aluminum titanate and mullite formed even at 1300 °C. The content of aluminum titanate increased in direct proportion to the amount of active additive introduced and the heat-treatment temperature. It should be noted that  $\gamma\text{-Al}_2\text{O}_3$  accelerated the mullite-forming reaction, while  $\alpha\text{-Al}_2\text{O}_3$  greatly facilitated the formation of aluminum titanate (Fig. 4); active fillers decreased the temperature of the latter reaction by 50 – 100 °C.

The crystal and porous structure of the composites determined the level of their physical – chemical and mechanical

properties. The introduction of active fibrous filler increased the porosity of the composites. As temperature increased to 1350 °C the porosity and water absorption of the ceramic decreased because of the formation of melt of aluminosilicate glasses, since the melt filled the pores in the material. For firing temperature 1380 – 1400 °C the fibrous powders formed with the matrix a rigid framework, which increased the strength of the composite material. The apparent density of the ceramic composites decreased somewhat with increasing temperature; this is due to the formation of mullite at 1300 – 1350 °C and aluminum titanate at 1350 – 1400 °C. The true density of these compounds equals, respectively, 3.17 and 3.70 g/cm<sup>3</sup>, while the true density of corundum and rutile is 4.00 and 4.25 g/cm<sup>3</sup>.

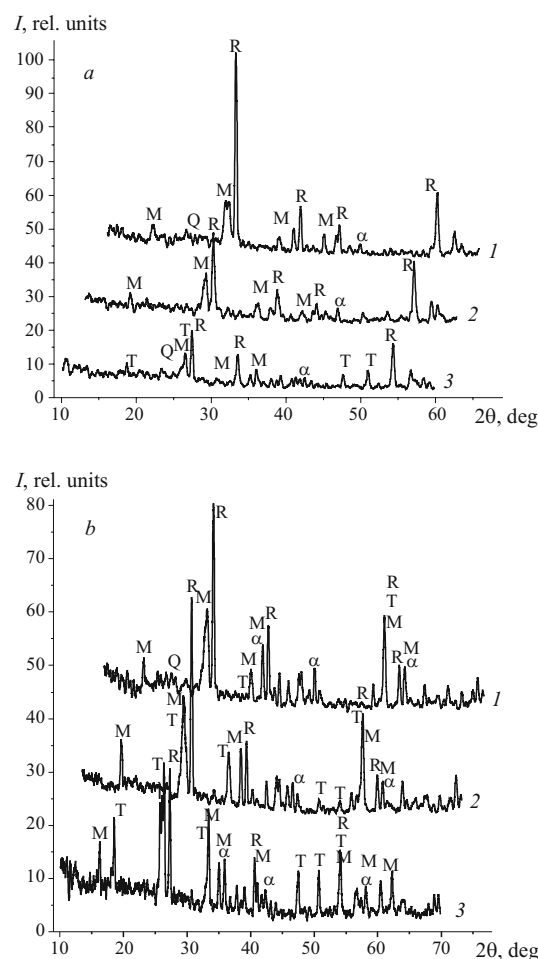


**Fig. 2.** Microstructure of the samples fired at 1350 °C: *a*)  $\gamma\text{-Al}_2\text{O}_3$  fibrous filler ( $\times 30,000$ ); *b*) matrices, mullite crystals are visible in a pore ( $\times 20,000$ ); *c*) composite with 20%  $\gamma\text{-Al}_2\text{O}_3$  filler ( $\times 20,000$ ).



**Fig. 3.** Variation of the integral intensities of the reflections of samples of composites, fired at 1300°C (a), 1350°C (b), and 1400°C (c) versus the content of the active filler  $\gamma\text{-Al}_2\text{O}_3$ : 1) tialite (020), 2) mullite (110), 3) corundum (113), 4) rutile (110).

The study of the mechanical properties of the composite shows that their strength was determined by the new phases formed and the contacts formed between the filler and the matrix when the ceramic materials are fired. The introduction of fibrous filler into the matrix increased the strength characteristics of the composites, since the fibrous particles served as centers for the dissipation of the energy of cracks developing under a thermal or mechanical shock. The highest bending strength was observed in composites with a low content of active fillers (5–10%) heat-treated at 1300–1350°C and composites containing 15–20% fillers fired at 1400°C (169–182 MPa). Since the nanostructural fillers in-



**Fig. 4.** X-ray diffraction patterns of the matrix (a) and composite with 20%  $\alpha\text{-Al}_2\text{O}_3$  (b), fired at temperatures 1300°C (1), 1350°C (2), and 1400°C (3): R) rutile, M) mullite, T) tialite;  $\alpha$ )  $\alpha\text{-Al}_2\text{O}_3$ ; Q) quartz.

creased the porosity of the material, its thermal conductivity decreases as a result of scattering of thermal phonons, but its thermal shock resistance increased since the possibility of stress relaxation under thermal loads increased.

Thermal shock resistance tests performed on the matrix and composites with active fillers established that the thermal shock resistance of the latter is higher. They withstood without crack formation more than 120 heating changes on heating to 800°C and cooling in flowing water (10°C). The shape and dimensions of the samples remained unchanged in the course of the tests.

In summary, the nanostructural fillers  $\gamma$ - and  $\alpha\text{-Al}_2\text{O}_3$  introduced into the ceramic matrix of the system  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--TiO}_2$  interacted with the matrix during firing, forming a mullite-tialite ceramic with enhanced strength and thermal shock resistance.

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